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GLAZED WALL CERAMICS WITH IMPROVED PHYSICOMECHANICAL AND DECORATIVE PROPERTIES

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A technology is developed for glazing wall ceramics using preliminary fusing of dried non-fired articles using a plasma torch with subsequent firing.

The construction materials with the best environmental, heat-shielding, and decorative characteristics in our country and abroad are ceramic bricks and stones. Special attention should be focused on facing, glazed and engobed wall ceramics which substantially improve the architectural and decorative aspects of modern buildings.

New types of wall materials with good physiochemical and decorative parameters are currently being developed. Thus, volume-tinted brick is produced on the basis of low-melting clays and finely disperse chalk [1]. A promising method involves the manufacture of face brick by double-layer compression, where the face side consists of light-burning clays from the Veselovskii deposit and quartz sand as the grog component [2]. Face bricks with decorative granular coating are produced by casting glaze slip using a disk sprayer, with subsequent drying and firing at temperature 950 – 980°C [3]. A rather efficient technology consists in decorating ceramic brick surface using the open flame of a gas burner [4]. Replacement the gas flame by a plasma torch significantly accelerates fusing of the brick surface, due to the high temperatures of the plasma (5000 – 10,000 K) [5]. However, local high-temperature heating of the wall ceramic surface, due to a significant thermal shock, weakens the surface layer, and cracks arise in it [5, 6]. This is the main cause for the decrease in the strength of adhesion of the fused layer to the substrate and decreased cold resistance, as well as emergence of stresses inside the coating. The fused layer that results is uneven and occasionally frothed, due to the high dynamic thrust of plasma-forming gases.

The present study represents the results of a study intended to eliminate the consequences of thermal shock during local high-temperature fusing of wall ceramic face surfaces by means of preliminary treatment of the dried product surface by a plasma torch and its subsequent firing.

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The initial samples were solid or hollow bricks 65 × 120 × 250 mm based on clay from the Polyana Ternovskoe deposit (Belgorod Region) and dried after plastic molding [7]. The face surface of the samples was treated by a GN-5r plasma burner of a UPU-8M plasma gun. The plasma gun functional parameters were as follows: working voltage 30 – 32 V, current 350 A. Argon was the plasma-forming gas; its consumption was 0.0014 g/sec under a pressure of 0.25 MPa. The distance from the plasma burner nozzle to the product surface was 15 mm. The speed of plasma treatment was 0.1 m/sec. In doing this, a glaze layer 1000 ± 200 μm thick was formed on the brick surface.

After fusing of the face surface, the samples underwent firing in a muffle furnace at a temperature 1273 K with exposure at the maximum temperature for 2 h. The finished glazed products were tested for cold resistance according to GOST 7025–91, the strength of adhesion of the glaze layer to the base was tested by the break-off method [8], and the porosity was tested using the "spot method."

Plasma fusing of non-fired samples leads to the emergence of stresses of the I and II kind in the surface layer. Moreover, due to the thermal shock, cracks arise in the fused glaze layer. A direct dynamic effect of the arc plasma current is to make the fused layer rough and frothed. However, under firing, the stresses in the fused surface layer relax, pores are fused over, and the diffusion zone between the crock and the vitreous phase expands. As a consequence, a smooth homogeneous glaze layer is formed, which has good physicomechanical and decorative properties.

The principle of elimination of the consequences of thermal shock in local high-temperature fusion of wall ceramic face surfaces to improve its physicomechanical and decorative properties is supported by USSR Author's Certificate No. 1116685. This principles makes it possible to use virtually any clay material suitable for wall ceramics according to GOST 530–95 for decorative purposes.

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TABLE 1

Treatment rate, m/sec	Glaze layer thickness, μm	State of glaze layer depending on moisture content of non-fired article			
		8%	10%	12%	14%
0.025	1400 ± 200	Exfoliation			
0.050	1100 ± 200	The same			
0.100	700 ± 100	Exfoliation is not observed	Exfoliation		
0.150	500 ± 100	Exfoliation is not observed		Exfoliation	
0.200	300 ± 100	Exfoliation is not observed			Exfoliation
0.250	150 ± 50	Exfoliation is not observed			

In the course of plasma melting of non-fired dried samples, the argillaceous materials are dehydrated, the crystal phases (mullite, hematite, quartz, cristobalite) are formed, and the vitreous phase emerges and accumulates. Simultaneously, a gas phase is formed, the vitreous phase diffuses into pores, and gas inclusions appear in the vitreous phase. The most critical is the dehydration phase, since it is then that the probability of formation of shrinkage cracks is heightened, whereas the conditions for crack healing are not yet provided. The water vapor of the residual moisture in the case of its high concentration in the pores of a dried sample can produce spontaneous exfoliation of the glaze layer.

The experiments revealed that when the surface of unfired samples with a high moisture content is fused using a plasma torch, the glaze layer becomes partly exfoliated from the substrate, due to the effect of thermal stresses and water vapor arising inside the pores of the article.

In order to optimize the technological parameters, the effect of the moisture content in non-fired bricks and the fusing rate on the state of the glaze layer was studied. A batch of standard-sized brick samples (65 × 120 × 250 mm) with moisture content of 8, 10, 12, and 14% was fused by a GN-5r plasma burner of a UPU-8M plasma gun with a treatment rate of 0.025 – 0.250 m/sec.

With a fusion rate of 0.025 – 0.050 m/sec, the glaze layer on samples with a normal moisture content of 8 – 10% becomes exfoliated. With fusion rates of 0.200 – 0.250 m/sec, no exfoliation of the glaze layer from the base is observed; however, since the thickness of the glaze layer is insignificant, it has poor decorative properties and a bumpy texture. It was concluded that the optimum fusion rate is 0.100 – 0.150 m/sec, when a glaze layer of sufficient thickness is formed and does not exfoliate from the substrate (Table 1).

The macrostructure was studied on transverse polished sections using a MBS-1 microscope in reflected light, as well as by differential thermal and x-ray phases analysis methods [8]. The fused glaze layer and the transition layer counting from the sample surface can be arbitrarily divided into 5 zones.

The first zone is represented mainly by the vitreous phase with occasional gas bubbles 50 – 100 μm in diameter and traces of the crystalline phase. With a fusion rate of 0.100 – 0.150 m/sec, this zone has a saturated light brown color and is 500 – 800 μm wide.

The second zone is black, frothed, and is located between the vitreous and a clearly defined crystalline zone of bright red (cream) color. The frothed zone is about 2000 μm wide and contains larger bubbles 250 – 500 μm in diameter. The phase composition of the frothed zone is represented by the vitreous phase (45 – 65%) and the crystalline phase (quartz, hematite, mullite).

The third one is the sintered crystalline zone represented by crystal phases (quartz, mullite, hematite) with an insignificant content of the vitreous phase (8 – 10%). Its thickness is 500 – 1000 μm.

The fourth zone has a pale pink color and consists mostly of the products of dehydration of clay minerals. Its phase composition is represented by quartz and x-ray-amorphous phases. This layer exhibits microcracks, and under a substantial thermal shock and a high moisture content, the fused glaze layer can exfoliate along these cracks.

The fifth is a transition zone which differs from the dried clay by a lighter shade. This zone contains dehydration products, as well as argillaceous materials mostly represented by kaolinite and hydromica. Dehydration processes start in the transition zone but are not completed, due to the short duration of the high-temperature effect. The width of this zone is 600 – 1000 μm. It also exhibits microcracks.

After firing of dried samples with the fused surface, the quality parameters of the glaze layer were tested using the standard methods [8, 9]. The studies indicated that the glazed wall ceramic exhibit sufficiently high quality parameters, which surpass similar parameters (cold resistance and adhesion strength) of articles produced using the current technologies of gas-torch and plasma-torch treatment of the face surface [4, 5, 7].

Properties of plasma-treated decorative coating with glaze layer thickness 1000 ± 100 μm

Strength of adhesion of glaze layer to substrate, MPa	3.8
Cold resistance, number of cycles	45
TCLE, 10^{-6} K^{-1}	4.5 – 6.7
Glaze layer density, g/cm^3	2.49 – 2.52

Refractive index	1.49 – 1.52
Fusibility of glaze layer vitreous phase, K	1673 – 1773
Microhardness, 10^3 MPa	5.52 – 5.68
Glaze layer porosity	Absent
Glaze layer surface texture	Uniform spreading
Presence in the glaze layer:	
of microcracks	None
of microchips	None
Presence of cracks between the glaze layer and the substrate	None

Thus, an efficient technology has been developed for producing glazed wall ceramics with good physiochemical and decorative properties through elimination of the consequences of thermal shock effects in high-temperature fusion of the face surface of articles using a plasma torch.

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